

The phi meter: A simple, fuel-independent instrument for monitoring combustion equivalence ratio

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An instrument has been developed to monitor the equivalence ratio in combustion systems. It is based on a novel oxygen consumption measuring method. The instrument does not require knowledge of the chemical composition of the process being monitored. Both gaseous and solid (soot) products of incomplete combustion are successfully handled. The device is relatively compact and can be developed for moderate cost and portable use.

I. INTRODUCTION

Gaseous carbon monoxide is mainly responsible for deaths due to unwanted fires.¹ This has been a major difficulty to specialists in fire protection engineering, since quantitative methods for predicting CO yields from building fires have not been available. Recent studies²⁻⁷ have indicated that the production of CO is primarily controlled by the equivalence ratio ϕ which is defined as

$$\phi = \left[\frac{\text{fuel}}{\text{oxygen}} \right] / \left[\frac{\text{fuel}}{\text{oxygen}} \right]_{\text{stoich}}, \quad (1)$$

where "stoich" denotes the stoichiometric fuel/oxygen ratio; it represents the actual fuel/oxygen ratio, compared to its stoichiometric value. Thus, $\phi < 1$ implies fuel-lean and $\phi > 1$ implies fuel-rich combustion. In the above definition, the oxygen includes only the oxygen atoms in oxidant (air, etc.) and not any oxygen atoms which would be present in the combustible species itself. Note that ϕ is independent of whether mass or molar quantities are taken.

Studies by Toner *et al.*³ on methane, Morehart *et al.*⁴ on methane and ethylene, and Beyler^{5,6} on hydrocarbons, alcohols, as well as several polymers, indicate an abrupt increase in the CO concentration by more than a factor of 10 as the global equivalence ratio increases from about 0.5 to 2. By "global," we mean here the overall equivalence ratio for the combustion process and not any spatial variations of fuel or oxygen concentrations. Beyler's^{5,6} studies also indicate that the CO yield is relatively insensitive to the fuel chemistry for global equivalence ratio in the range 1.5–2.0. Experimental fire tests with building materials⁷ have suggested that, under certain circumstances, the yield of CO from a fire is determined only by the overall ϕ of the process, with the actual chemical nature of the fuel in question being unimportant. Recent studies⁸ indicate that a simple relationship of CO yield on the global equivalence ratio (GER) may not be applicable in the cases where the fuel is situated primarily in the uppermost portions of the fire compartment; compartment temperature is also seen to play some role. Nonethe-

less, the GER theory is very promising to practical predictions of CO.

It is probable that over the next few years substantially more work will be done to further quantify and extend the GER concept. Up until now, however, the concept could only be used in situations where fuel and air flows could be accurately metered and the chemical composition of the fuel was known. This can be arranged during controlled experiments using gas burners or liquid fuels. Even in such experiments, however, accurate determination of air flows at room openings can be problematic due to low flow velocities and flow nonuniformities.⁹ For fire safety purposes, solid combustibles are of greatest concern, unfortunately, their burning rate cannot be either controlled or accurately measured. Thus, there is a need for an instrument which can make an *in situ* ϕ measurement, that is, a phi meter. By obtaining data of CO yield versus ϕ , the GER concept can be tested.

The widest range of applications for the phi meter is probably industrial. Even for well-instrumented industrial power plant facilities with multiple gas detectors, it would be advantageous to have a single instrument to monitor combustion efficiency. The phi meter would be useful for monitoring ϕ at incineration facilities, which may have a complicated mix of household and industrial wastes. A portable version could be used to monitor wood burning stoves. Also, there are industrial processes whose success depends on operating fuel rich in a narrow range of ϕ . These processes include the reduction of NO_x emission by running power plants fuel rich at one stage, the production of carbon black, and recent developments in producing advanced materials including fullerenes and diamond films.

II. PRINCIPLES OF THE PHI METER

If the fuel does not contain oxygen atoms, a value of ϕ can be computed by carrying out a complete analysis of all the significant combustion products. The computation is based on conservation of C, H, and O atoms in the combustion reaction. (The small fraction of C and H present in normal air can either be ignored or corrected for.) For most systems, however, this will require a large number of gas analyzers, making the method neither portable nor simple.

The number of gases to be analyzed, however, can be decreased by introducing a combustion system into the gas

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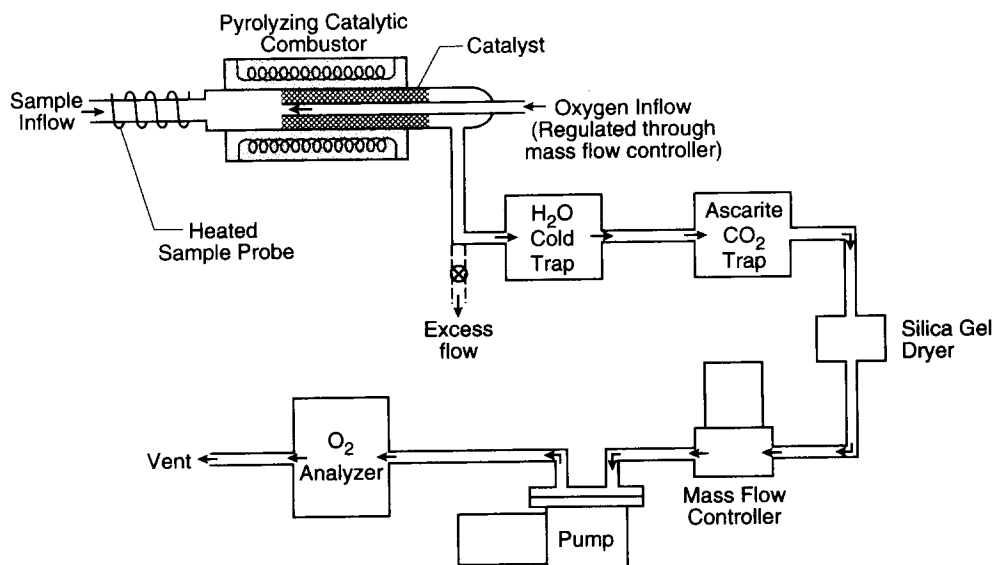


FIG. 1. Schematic of the phi meter. The excess-gas flow piping (shown dotted) is pertinent only to certain calibration experiments and is not a standard operating feature of the instrument.

train. By passing the combustion gases through a heated catalyst, it is possible to reduce the number of ultimate gases to be analyzed to just CO_2 , H_2O , and O_2 . In the general case of fuel-rich mixtures, this will also require an additional oxygen stream to be introduced to ensure the completion of the combustion. The resulting system, while simpler, is still cumbersome. The need for three gas analyzers still makes this a relatively large and costly approach. Especially troublesome is the measurement of H_2O . In our experience at NIST, only infrared H_2O analyzers are able to accurately measure H_2O concentrations continuously in combustion gas streams. Even so, the required heated-line plumbing is troublesome and difficult to maintain.

The solution was found to lie in a scheme where only an oxygen analyzer is needed. Such an approach offers the potential of easy operation, low cost, and portability. The measuring principle to be described has been termed the oxygen consumption method. It represents a novel extension of a concept earlier developed to sense indirectly the heat released from combustion processes.¹⁰⁻¹² The basic concept is that, as in the scheme outlined above, a combustor is used to burn all of the carbon atoms in the fuel to CO_2 and all of the hydrogen atoms in the fuel to H_2O . With the scheme to be described below, the oxygen concentration with the combustion tube in place is measured: (a) for the ambient air without oxygen addition, (b) for ambient air with oxygen addition, and (c) for the sampled combustion products with oxygen addition. Analysis of these measurements then yields ϕ .

Figure 1 shows the schematic of the apparatus. The probe is inserted into the atmosphere to be sampled using a sampling line (0.95 cm o.d.) heated to about 100°C to avoid the condensation of moisture and condensable hydrocarbons and to minimize thermophoretic deposition of smoke particulates. In general, a soot filter should *not* be used in this line, since reaction products showing up as soot must be recombusted and quantified, not ignored. The sampling line leads

to a cylindrical tube furnace heated to approximately 1000°C . The tube furnace is 2.5 cm in diameter and 80 cm long, corresponding to a volume of 420 cm^3 . The inner oxygen tube is 1.25 cm in diameter and extends to about the center of the tube furnace. The opening of the tube is covered with a platinum screen and about 6 m of 0.2 mm diameter platinum wire is wrapped uniformly along the tube. The chamber is packed with gauze, beads, or other forms of combustion catalyst. Platinum gauze was used in our studies; palladium is another suitable catalyst. An inlet stream of pure oxygen, supplied from a bottled source, is also led into the tube furnace. The oxygen flow was nominally 0.25 l/min ($4.2\text{ cm}^3/\text{s}$) and the flow through the oxygen analyzer was about 0.5 l/min ($8.3\text{ cm}^3/\text{s}$). From the tube furnace, the gas is passed through a thermoelectric cold trap with a volume of about 70 cm^3 , an Ascarite CO_2 trap with a 400 cm^3 volume, and an additional desiccant medium (silica gel) just before the oxygen analyzer. It then goes through a mass flow controller and into a paramagnetic oxygen analyzer. There is a 75 s delay time from entrance into the combustion tube to arrival at the oxygen meter followed by a 65 s response time to reach 95% of the final value. A predecessor version to the combustion system used in the phi-meter apparatus was used in studying the thermal decomposition of wood.¹³

III. SOLUTION FOR THE EQUIVALENCE RATIO

The basic relationship for ϕ is expressed in Eq. (1). The simplest situation is one where the reactants are unburned (but fully mixed) prior to entering the tube furnace and there is no additional oxygen introduced. The basic geometry can be envisioned as two flow streams being mixed prior to entry into the tube furnace. One stream comprises the flow rate of the fuel, \dot{n}_f . The second stream has two components, oxygen and nitrogen: $\dot{n}^0(\text{O}_2)$ and $\dot{n}^0(\text{N}_2)$. Then, ϕ is

$$\varphi = \left(\frac{\dot{n}_f}{\dot{n}^0(\text{O}_2)} \right) \bigg/ \left(\frac{\dot{n}_f}{\dot{n}_r(\text{O}_2)} \right), \quad (2)$$

where \dot{n}_f is the molar flow of fuel, $\dot{n}^0(\text{O}_2)$ is the ambient molar flow of oxygen, and $\dot{n}_r(\text{O}_2)$ is the molar flow of oxygen required for complete stoichiometric combustion. The latter, in turn, is given by

$$\dot{n}_r(\text{O}_2) = \dot{n}^0(\text{O}_2) - \dot{n}(\text{O}_2), \quad (3)$$

where $\dot{n}^0(\text{O}_2)$ denotes the ambient oxygen molar flow rate, while $\dot{n}(\text{O}_2)$ is the exhaust molar oxygen flow rate. Combining the above two equations, gives

$$\varphi = \frac{\dot{n}^0(\text{O}_2) - \dot{n}(\text{O}_2)}{\dot{n}^0(\text{O}_2)}. \quad (4)$$

The nitrogen does not participate in the combustion reaction, thus the flow rate of nitrogen is identical into the combustor and out of it. Dividing through by the nitrogen flow rate and making use of the fact that

$$\dot{n}^0(\text{N}_2) = \dot{n}(\text{N}_2) \quad (5)$$

gives

$$\varphi = \left(\frac{\dot{n}^0(\text{O}_2)}{\dot{n}^0(\text{N}_2)} - \frac{\dot{n}(\text{O}_2)}{\dot{n}(\text{N}_2)} \right) \bigg/ \left(\frac{\dot{n}^0(\text{O}_2)}{\dot{n}^0(\text{N}_2)} \right). \quad (6)$$

Since the ratio of molar flows is equal to the ratio of molar fractions, we can express Eq. (6) in terms of the mole fractions X_{O_2} and X_{N_2} ,

$$\varphi = \left(\frac{X_{\text{O}_2}^0}{X_{\text{N}_2}^0} - \frac{X_{\text{O}_2}}{X_{\text{N}_2}} \right) \bigg/ \left(\frac{X_{\text{O}_2}^0}{X_{\text{N}_2}^0} \right), \quad (7)$$

where $X_{\text{O}_2}^0$ denotes the ambient oxygen mole fraction ($=0.21$). Noting that H_2O and CO_2 have been trapped out of the gas stream presented to the gas analyzer, for any set of conditions,

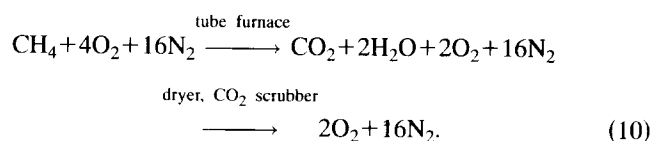
$$X(\text{O}_2) + X(\text{N}_2) = 1. \quad (8)$$

Then,

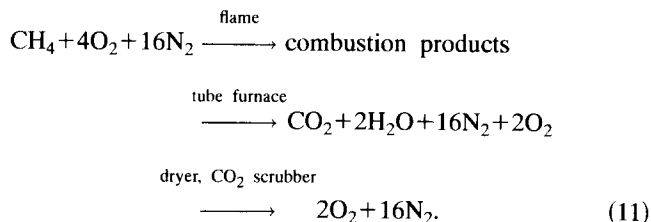
$$\varphi = 1 - \left[\frac{X_{\text{O}_2}}{X_{\text{O}_2}^0} \right] \frac{1 - X_{\text{O}_2}^0}{1 - X_{\text{O}_2}}. \quad (9)$$

As a consistency check on Eq. (9), we consider the two extremes of X_{O_2} equals $X_{\text{O}_2}^0$ and 0. This leads to the expected results of $\varphi=0$ and $\varphi=1$, respectively.

As an example, we consider methane entering at 1 mol/s, oxygen at 4 mol/s, and nitrogen at 16 mol/s. The changes in the gas composition resulting from going through the combustor and then the dryer and the scrubber are expressed as follows:



In this example, $\dot{n}^0(\text{O}_2)$ is 4 mol/s and $\dot{n}(\text{O}_2)$ is 2 mol/s, so from Eq. (4), $\varphi=0.5$. Next, we consider the case where the methane and air burn before being sampled by the phi meter. So in this case Eq. (10) is modified to read



In this case, $\dot{n}^0(\text{O}_2)$ is the molar flow of oxygen into the flame, which we will term the ambient oxygen flow, and is not the molar flow of oxygen in the combustion products going to the tube furnace. Thus, φ is determined by the same procedure as if the fuel and oxygen had not reacted before entering the combustor.

The above derivation assumed that only systems with $\varphi < 1$ are being studied. In actual fact, of course, the fuel-rich regime also needs to be characterized. For this, the supplemental "oxygenator" stream is used. The molar flow of oxygen in the oxygenator stream is defined as $\dot{n}^a(\text{O}_2)$. In this case, the expression for the molar flow of oxygen for complete combustion, $\dot{n}_r(\text{O}_2)$, given by Eq. (3) has an additional term:

$$\dot{n}_r(\text{O}_2) = \dot{n}^a(\text{O}_2) + \dot{n}^0(\text{O}_2) - \dot{n}(\text{O}_2). \quad (12)$$

This, in turn, results in an additional term in the expression for φ compared to Eq. (6). The second and third terms in Eq. (13) correspond to the φ given by Eq. (9). The first term in Eq. (13) is defined as φ_1 and it will be shown below how φ_1 can be expressed in terms of oxygen volume fractions.

$$\varphi = \left(\frac{\dot{n}^a(\text{O}_2)}{\dot{n}(\text{N}_2)} + \frac{\dot{n}^0(\text{O}_2)}{\dot{n}^0(\text{N}_2)} - \frac{\dot{n}(\text{O}_2)}{\dot{n}(\text{N}_2)} \right) \bigg/ \left(\frac{\dot{n}^0(\text{O}_2)}{\dot{n}^0(\text{N}_2)} \right). \quad (13)$$

Using the ideal gas law, $\dot{n}^a(\text{O}_2)$ and $\dot{n}(\text{N}_2)$ can be expressed in terms of the volumetric flow of added oxygen, V_a , and the total volumetric flow to the oxygen analyzer, V :

$$\dot{n}^a(\text{O}_2) = \frac{V_a P_a}{RT_a}, \quad (14)$$

$$\dot{n}(\text{N}_2) = \frac{VP(1 - X_{\text{O}_2})}{RT}. \quad (15)$$

Using Eqs. (14) and (15), φ_1 can be expressed as

$$\varphi_1 = \left(\frac{\dot{n}^a(\text{O}_2)}{\dot{n}(\text{N}_2)} \right) \bigg/ \left(\frac{\dot{n}^0(\text{O}_2)}{\dot{n}^0(\text{N}_2)} \right) = \frac{(1 - X_{\text{O}_2}^0)V_a P_a T}{X_{\text{O}_2}^0(1 - X_{\text{O}_2})VPT_a}, \quad (16)$$

where the following relationship is used for the denominator in Eq. (13):

$$\frac{\dot{n}^0(\text{O}_2)}{\dot{n}^0(\text{N}_2)} = \frac{X_{\text{O}_2}^0}{1 - X_{\text{O}_2}^0}. \quad (17)$$

The volumetric flow ratio V_a/V can be expressed in terms of the ambient volume fraction of O_2 and of the volume fraction

of O_2 at the O_2 analyzer for the case of ambient air at the inlet, $X_{O_2}^i$. It is assumed that the temperature and pressure are the same for the oxygenator and the oxygen analyzer. Then, from the definition of volume fraction, $X_{O_2}^i$ can be related to the flow ratio: We note here that $X_{O_2}^i$ is defined for a particular total volume flow through the analyzer. This volume flow must remain constant during the test for the following equations to apply. Solving then for V_a/V ,

$$X_{O_2}^i = \frac{V_a + (V - V_a)X_{O_2}^0}{V} = \frac{V_a}{V} (1 - X_{O_2}^0) + X_{O_2}^0, \quad (18)$$

$$\frac{V_a}{V} = \frac{X_{O_2}^i - X_{O_2}^0}{1 - X_{O_2}^0}. \quad (19)$$

The quantity φ_1 is obtained by substituting the expression for the flow ratio given by Eq. (19) into Eq. (16):

$$\varphi_1 = \frac{X_{O_2}^i - X_{O_2}^0}{X_{O_2}^0(1 - X_{O_2}^0)}. \quad (20)$$

The expression for φ is obtained for the case of added oxygen by adding the expression given in Eq. (9), which corresponds to no O_2 added, to that for φ_1 , given in Eq. (20):

$$\varphi = 1 - \frac{X_{O_2}(1 - X_{O_2}^0)}{X_{O_2}^0(1 - X_{O_2}^0)} + \frac{X_{O_2}^i - X_{O_2}^0}{X_{O_2}^0(1 - X_{O_2}^0)} = \frac{X_{O_2}^i - X_{O_2}}{X_{O_2}^0(1 - X_{O_2}^0)}. \quad (21)$$

The corresponding expression in terms of volumetric flow rate, for later reference, is obtained from Eqs. (9) and (16) as

$$\varphi = 1 - \left[\frac{X_{O_2}}{X_{O_2}^0} \right] \frac{1 - X_{O_2}^0}{1 - X_{O_2}} + \frac{(1 - X_{O_2}^0)V_a}{X_{O_2}^0(1 - X_{O_2})V}. \quad (22)$$

It is important to note here that in Eq. (21) only three pieces of data are required: the base line oxygen concentration without oxygenator ($X_{O_2}^0$), the base line oxygen concentration with the oxygenator ($X_{O_2}^i$), and the oxygen concentration under combustion conditions (X_{O_2}). It may be noted that the volumetric flow does not require monitoring but it must remain constant.

In the derivation of Eq. (21) it was assumed that the volume flow remained constant. However, the typical mass flow controller actually produces a constant enthalpy flow. Heat is delivered to the stream at a constant rate and the flow is controlled to produce a constant temperature rise. As long as the molar heat capacity of the fluid is invariant, as it would be for a flow of fixed chemical composition, this also ensures a constant volume flow rate. The fluid passing through the oxygen analyzer is a mixture of oxygen and nitrogen with the oxygen concentration varying from $X_{O_2}^i$ to 0. Since the molar heat capacities of oxygen and nitrogen are similar, the volume flow is nearly constant so that Eq. (21) is a good approximation for most applications. However, this equation can be readily expanded to deal with constant enthalpy rather than constant volume flows.

For constant enthalpy flow,

$$\left(\frac{C_{O_2}}{C_{N_2}} X_{O_2} + 1 - X_{O_2} \right) V = \text{constant}, \quad (23)$$

where C_{O_2} and C_{N_2} are the constant-pressure specific heats. Because the flow is now allowed to vary, the volume flow, V , in Eqs. (18) and (19) must be regarded only as its value with ambient air at the inlet and should be designated as V^i . Then, using Eq. (23), the following expression is obtained for the flow ratio, V^i/V , which is denoted as β :

$$\frac{V^i}{V} = \beta = \frac{1 - [1 - (C_{O_2}/C_{N_2})]X_{O_2}}{1 - [1 - (C_{O_2}/C_{N_2})]X_{O_2}^i}. \quad (24)$$

Assuming again that the temperature and pressure are essentially constant, Eq. (16) can be written as

$$\varphi_1 = \frac{(1 - X_{O_2}^0)}{X_{O_2}^0(1 - X_{O_2}^0)} \frac{V_a}{V^i} \frac{V^i}{V}. \quad (25)$$

Substituting β for V^i/V and Eq. (19) for V_a/V^i , φ_1 is given by

$$\varphi_1 = \frac{\beta(X_{O_2}^i - X_{O_2}^0)}{X_{O_2}^0(1 - X_{O_2}^0)}. \quad (26)$$

The equivalence ratio φ is obtained from Eq. (22) by replacing the third term on the right hand side, which is equal to φ_1 , with the expression in Eq. (25). The final result can be expressed in the following compact form:

$$\varphi = \frac{\beta(X_{O_2}^i - X_{O_2}^0) + X_{O_2}^0 - X_{O_2}}{X_{O_2}^0(1 - X_{O_2}^0)}. \quad (27)$$

Note that Eq. (27) reduces to Eq. (21) when $C_{O_2} = C_{N_2}$.

IV. OPERATING RANGE

For an instrument based on this concept to be viable, it first had to be demonstrated that the range of φ values encompassed is acceptably broad to be useful in practical work. For the study of CO toxicity in unwanted fires, a range of $0.5 \leq \varphi \leq 2.5$ encompasses the regime of primary interest. The upper end will rarely exceed 3.0, because combustion that is so fuel-rich is normally difficult to sustain. At the low end, some very dilute processes can possibly be of interest; as will be shown, for such situations the phi meter would not be suitable. For most other uses, however, the operating range will be seen to be adequate.

The upper limit to φ values that can be measured is set simply by the oxygenation level. By setting $X(O_2) = 0$ in Eq. (21), one obtains the following expression for φ_{\max} :

$$\varphi_{\max} = \frac{X_{O_2}^i}{X_{O_2}^0}. \quad (28)$$

Thus, if $X_{O_2}^0 = 0.21$ and it is desired to measure up to a maximum of $\varphi = 3.0$, the oxygenator flow must be sufficient to set $X_{O_2}^i = 0.63$ (in practice, higher than 0.63, to ensure complete conversion of the incomplete products of combustion to CO_2 and H_2O). At the low- φ end, the limits to the

operating range are set by the accuracy of the oxygen meter as discussed in the uncertainty analysis. For $X_{O_2}^i = 0.75$, the phi-meter range of operation is from 0.3 to 3.0 with the highest precision for the largest ϕ . By changing the value of $X_{O_2}^i$, the minimum value of ϕ could be reduced to about 0.1 ($X_{O_2}^i = 0.24$) or increased to about 4.0 ($X_{O_2}^i = 0.87$).

V. RANGE OF FUELS

The phi meter as described above will apply to fuels containing C, H, and O, since the products of complete combustion consist of only CO_2 and H_2O , which will be scrubbed from the system. There is a range of common engineering plastics of interest to fire safety that contain additional elements. They include Cl in polyvinylchloride (PVC), N in polyurethane, F in polytetrafluoroethylene, and S in polysulfonates. Our analysis is based on the assumption that only O_2 and N_2 are present in the O_2 analyzer and that all other gases have been scrubbed out. The scrubber selected for removing CO_2 may also be effective in removing other products of combustion such as Cl_2 and HCl from PVC and oxides of nitrogen and sulfur that might be produced by the combustion of polyurethane and polysulfonates. Additional scrubbers may be needed for special applications. Any (unusual) combustion process which would produce large amounts of N_2 as a combustion product would not be subject to analysis, since the assumption is made that N_2 is not produced in the fire or in the tube furnace.

VI. AN ALTERNATE CLOSED-LOOP ARRANGEMENT

The bulk of the development work done at NIST on the phi meter has been carried out under the conditions as described above. One limitation to the system is that the output is not direct reading, but one requiring a nonlinear computation (albeit a fast and noniterative one). A somewhat different arrangement is possible whereby the sensing element is placed in a closed loop, controlling the flow rate of the oxygenator. This application would resemble in certain features an isothermal heat release rate calorimeter earlier developed at NIST.¹⁴ In the present case, the oxygen analyzer would function as the sensing element and the system would be set up to have the feedback loop add enough oxygen to always maintain the oxygen analyzer reading at its setpoint value.

The equation describing this arrangement is especially simple. It is obtained from Eq. (22) for the case that $X_{O_2} = X_{O_2}^0$:

$$\phi = \frac{V_a}{X_{O_2}^0 V}, \quad (29)$$

where V is the volume flow through the oxygen analyzer, V_a is the volume flow of oxygen being supplied by the oxygenator, and $X_{O_2}^0$ is the ambient oxygen molar fraction. Such an arrangement would be direct reading in the value of ϕ which, apart from constants, would be proportional to the voltage being sent to the flow controller controlling the supply of the

TABLE I. Experimental efficiency in oxidizing 35 nm average-diameter soot particles for various residence times using 1000 °C tube furnace conditions.

| Residence time (s) | Fraction of soot oxidized to gases |
|--------------------|------------------------------------|
| 30 | 0.95–1.0 |
| 15 | 0.70–0.90 |
| 7.5 | 0.50–0.70 |

supplemental oxygen. For the development of this alternative to be practical, system delay times would need to be carefully adjusted to avoid control instabilities.

VII. EXPERIMENTAL

A. Residence time

It was considered essential that the phi meter be capable of combusting not only gaseous products of incomplete combustion but also solids, that is, soot. Thus, a preliminary study was carried out to determine if the concept was feasible under conditions of an acceptably short residence time (which is defined as the gas flow time during which the gas sample is flowing through the heating zone of the combustor). The requirements for the residence time and for the operating temperature are interrelated: as the soot particle size is increased, more residence time, a higher operating temperature, or both are required.

To test out the residence time and combustor temperature needed, a coannular diffusion burner was constructed, fueled with acetylene. The mass generation rate of soot from this generation method was quantified using a tapered-element oscillating microbalance (TEOM). A fraction of the soot output from the burner was drawn through the combustion tube, through a tube connecting the TEOM and the combustion tube, and into the TEOM. The experiments were conducted by setting the combustor temperature to 1000 °C and by varying the residence time. The fraction of soot oxidized to gases was computed based on the TEOM measurement of the soot concentration for the heated and unheated tube. As the soot leaves the combustion tube at 1000 °C, it rapidly cools to near-ambient temperature before reaching the TEOM. The large temperature gradient results in thermophoretic deposition of the soot particulates on the walls of the tube. In computing the fraction of soot oxidized to gases we estimate that 50% of the soot particulates were lost to the walls by thermophoresis. This estimate is based on previous measurements on the effect of the inlet gas temperature on the particle deposition in a tube. The experimental results are given in Table I.

It is also possible to compute a theoretically predicted time to oxidize a soot spherule. According to the Nagle Strickland–Constable theory, the oxidation of a spherule of initial diameter D_i proceeds according to

$$D = D_i - 2wt/\rho, \quad (30)$$

where D is the diameter after the combustion process, and this should approach zero if the combustor operation is satisfactory. The residence time is t , while ρ is the density, taken as 2000 kg m⁻³. The oxidation rate w was taken¹⁵ as

TABLE II. Theoretical reduction in sphere diameter due to a 30 s residence time at various combustion temperatures.

| Temperature (°C) | $D_i - D$ (nm) |
|------------------|----------------|
| 700 | 7 |
| 800 | 40 |
| 900 | 150 |
| 1000 | 470 |
| 1100 | 1260 |

$113 \exp(-E/RT) \text{ kg m}^{-2} \text{ s}^{-1}$, with the activation energy E taken as 143 kJ mol^{-1} . According to the above equation, for a residence time of 30 s, the relationship of combustor temperature to maximum sphere diameter to be completely burned can be computed and this is shown in Table II.

The primary spherule size being generated by the acetylene burner generation scheme was measured with transmission electron microscopy and determined to be approximately 35 nm. The predicted results suggest that for a 30 s residence time a minimum temperature of 800 °C would be adequate to oxidize the soot. Experimentally, it was found that a higher temperature of 1000 °C (which is easily attainable in normal practice) was necessary to complete gasification of the soot. Thus, the experimental results (Table I) are reported at a temperature of 1000 °C.

B. Methane calibration

The first step in actually checking out the operating principle of the phi meter was to meter in individual flows of methane, oxygen, and nitrogen. In such an arrangement, external combustion is not used at all and the 100% unburnt fuel is presented to the phi meter. A direct determination of the actual ϕ is available, due to the known flow rates. Based on flow calibrations using either the soap film method or a dry test meter, we estimate fractional systematic uncertainties, $\delta V_{\text{air}}/V_{\text{air}}$ and $\delta V_{\text{methane}}/V_{\text{methane}}$, for both fuel and air as ± 0.02 . The imprecision for repeat flow settings calibrations divided by the flow is estimated to be ± 0.01 . The effect of these uncertainties on the uncertainty in ϕ is computed in a separate section below.

Equations (21) and (22) assume a constant outlet flow, while for this calibration the inlet flow is constant. In this case the appropriate equation, which is derived in the Appendix, is given by

$$\phi = 1 - \left[\frac{X_{\text{O}_2}}{X_{\text{O}_2}^0} \right] \frac{1 - X_{\text{O}_2}^0}{1 - X_{\text{O}_2}} + \frac{X_{\text{O}_2}^i - X_{\text{O}_2}^0}{X_{\text{O}_2}^0 (1 - X_{\text{O}_2}^i)} \quad (31)$$

The value of ϕ inferred from the X_{O_2} measurements together with Eq. (28) is compared with ϕ computed based on the inlet flow of oxygen and methane in Fig. 2; the agreement between the two is seen to be excellent.

In the next step of the experimental study, an external combustion system was set up. Air and methane were metered into a premixed burner. A fraction of the combustion gases leaving the burner was drawn into the phi-meter sampling port. As would be expected, combustion of the external burner could not be maintained under excessively lean or rich equivalence ratios. The points are indicated in Fig. 3

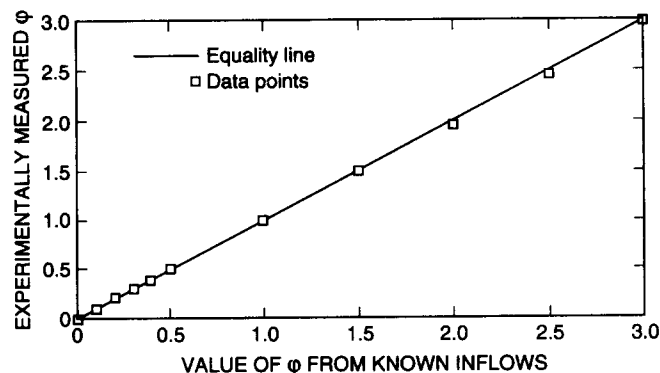


FIG. 2. Comparison of directly computed ϕ against its value as determined from Eq. (21). Methane is the fuel gas. There is no external combustion; all combustion takes place within the combustor of the phi meter only.

where external combustion was sustained. For the remaining data points, the only reaction taking place was within the phi meter. For both conditions, good agreement between the calibrated flows and the measurements is seen. It can also be seen that there is no deviation in trends between points where external combustion was sustained versus those where it was not.

The methane flame used produced only a small amount of soot. Thus, the next series of experiments undertaken were using acetylene as the fuel gas.

C. Acetylene calibration

To calibrate with acetylene quantitatively, it was necessary to devise a scheme whereby excessive soot losses would not occur prior to the products entering the phi meter. The method adopted is shown in Fig. 4. The actual air-acetylene flame was established directly within the inlet region of the phi meter's tube furnace. Two variant experimental series were conducted. In the first, the inlet tube of the phi meter was closed with a stopper so that the inflows were exactly known. The excess-gas discharge (dotted lines in Fig. 1) was needed for this configuration. In the second series, the stopper was removed and the excess-gas discharge port was closed. Theoretical values of ϕ could still be known since the

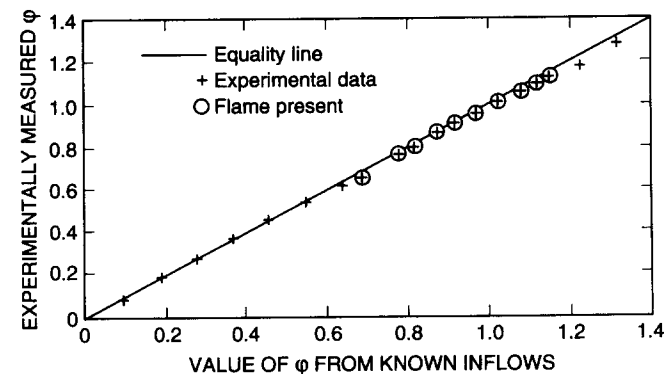


FIG. 3. Comparison of directly computed ϕ against its value as determined from Eq. (21). Methane is supplied to an external premixed burner; the products of combustion are sampled by the phi meter.

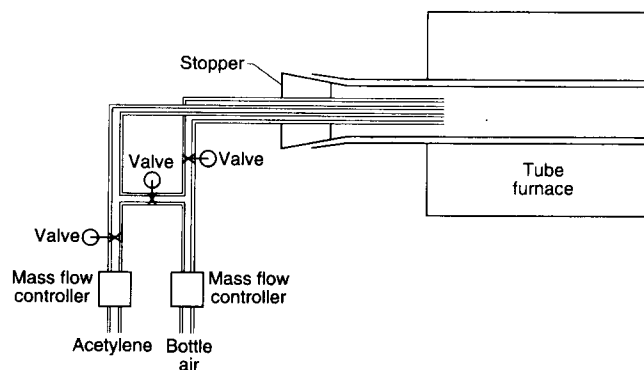


FIG. 4. Experimental arrangement used for acetylene flame calibrations.

amounts of fuel and air flow were such that there was a net spillage to the outside occurring at the phi-meter inlet, not a sucking in of room air. It is believed that the slight systematic shift from the equality line in Fig. 5 was due to acetylene calibrations of the fuel supply flow controller having been less accurate than those for methane. The curvature seen for the highest φ values possibly represents the beginning of soot breakthrough. Acetylene was deliberately selected as having the sootiest combustion products that could readily be generated. Burning it in the regime of $\varphi > 2$ constitutes exceedingly fuel-rich, soot-laden conditions.

D. Tests in reduced-scale fire test room

An experimental room was constructed at NIST which represents a 2/5 scale model of a fire test room most commonly used in U.S. practice.¹⁶ Fires of natural gas, hexane, and wood were studied in this environment. The range of heat release values examined covered from 7.5 to 600 kW. The phi meter was seen to give satisfactory performance over the range of conditions studied. For these 1–2 h experiments, the Ascarite CO₂ trap was replaced with a 250 ml gas scrubber bottle filled with 2 M NaOH to overcome clogging problems experienced with the Ascarite trap that was used. The use of a fine glass frit to produce small bubbles removed

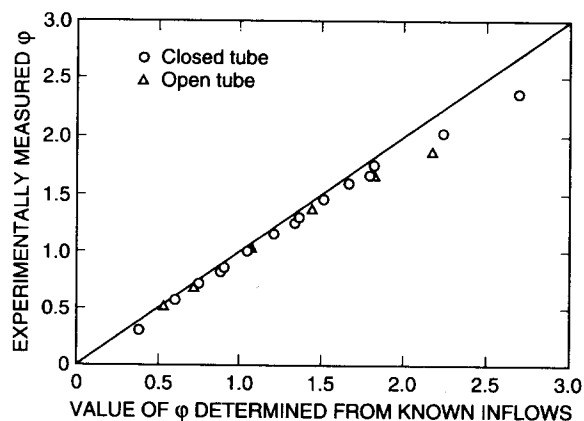


FIG. 5. Comparison of directly computed φ against its measured value. Equation (31) was used for the closed-tube experiments, while Eq. (21) was used for the open tube configuration. Acetylene is the fuel gas, burned in the arrangement shown in Fig. 4.

TABLE III. Uncertainty analysis for φ with $X_{O_2}^i = 0.63$.

| φ | X_{O_2} | $u(O_2^i)/\varphi^a$ | $u(O_2)/\varphi$ | U/φ^b |
|-----------|-----------|----------------------|------------------|---------------|
| 0.1 | 0.622 | ± 0.250 | ± 0.245 | ± 0.568 |
| 0.5 | 0.587 | ± 0.047 | ± 0.042 | ± 0.108 |
| 1.0 | 0.532 | ± 0.020 | ± 0.016 | ± 0.050 |
| 1.5 | 0.460 | ± 0.012 | ± 0.008 | ± 0.032 |
| 2.0 | 0.362 | ± 0.007 | ± 0.004 | ± 0.024 |
| 2.5 | 0.221 | ± 0.005 | ± 0.002 | ± 0.018 |
| 3.0 | 0.000 | ± 0.003 | ± 0.001 | ± 0.014 |

^aThe symbols $u(O_2)$ and $u(O_2^i)$ refer to the uncertainties in $X(O_2)$ and $X(O_2^i)$, respectively.

^bThe symbol U refers to the expanded uncertainty (95% confidence interval) in the measurement of φ .

essentially all of the CO₂. Since the main purpose of these experiments, however, was not to calibrate the phi meter but to already use it as a measuring tool, details of results are being reported separately.⁸

E. Uncertainty analysis

The determination of the uncertainty in φ requires estimates of the experimental imprecision and the systematic uncertainties associated with the measurement of X_{O_2} and $X_{O_2}^i$. From repeat measurements, we estimate the imprecision to be ± 0.02 . The systematic uncertainties are estimated by computing the logarithmic derivative, $\partial(\ln \varphi)/\partial p_i$, where the parameter p_i represents $X(O_2)$ and $X^i(O_2)$. We obtain the following results for the uncertainties $u(O_2)$ and $u(O_2^i)$, where u denotes the uncertainty in a given variable:

$$\frac{u(O_2^i)}{\varphi} = \frac{\delta_{O_2}^i}{X_{O_2}^i - X_{O_2}}, \quad (32)$$

$$\frac{u(O_2)}{\varphi} = \frac{-\delta_{O_2}(1 - X_{O_2}^i)}{(1 - X_{O_2})(X_{O_2}^i - X_{O_2})}. \quad (33)$$

We operate the phi meter with $X_{O_2}^i = 0.63$, and we estimate the uncertainty in the paramagnetic oxygen analyzer, $\delta(O_2)$ and $\delta(O_2^i)$, as ± 0.002 . The computed values of the uncertainties as a function of φ are given in Table III. The combined uncertainty, u_c , is obtained by adding in quadrature the imprecision to 1/3 the sum of the systematic uncertainties.

$$u_c = \{u_i^2 + (1/3)[u(O_2)^2 + u(O_2^i)^2]\}^{1/2}. \quad (34)$$

We obtain an expanded uncertainty, U , corresponding to the 95% confidence interval by multiplying u_c by a factor of 2. As indicated in Table III, the expanded uncertainty for $\varphi=1$ is ± 0.05 . The uncertainty for large φ is determined by the imprecision, while for small φ the accuracy of the oxygen analyzer is also important.

We can perform an analogous uncertainty analysis for φ based on the flows of air and fuel. The systematic uncertainties, $\delta V_{\text{air}}/V_{\text{air}}$ and $\delta V_{\text{methane}}/V_{\text{methane}}$, are combined with the imprecision, which in this case is the standard error, to give $u_c(\text{flow})/\varphi = \pm 0.019$ and $U(\text{flow})/\varphi = \pm 0.038$. The results in Figs. 2 and 3 are generally consistent with the predicted uncertainties. The predicted uncertainties are largest for small φ , though such an effect is not apparent from the data. A

possible explanation is that the low φ measurements were made just after measuring $X_{O_2}^i$ so instrument drift was a minor factor for these measurements. The measured φ for acetylene in Fig. 5 underestimates the correct φ by more than the predicted uncertainty. The larger discrepancy may be a result of smoke penetration through the combustion tube which is not included in the uncertainty analysis.

VIII. PRACTICAL CONSIDERATIONS

The basic size of the instrument is determined by the type of oxygen analyzer used. The system can be substantially reduced in physical size and sample gas flow requirements by selecting an oxygen analyzer with low flow requirements. Precision paramagnetic oxygen detectors are now commercially available which require only a ~ 1.3 cm³/s flow. This is compatible with a 10%–90% rise time of < 4 s. The sizing of the system then proceeds from the requirement of a 30 s residence time.

The experimental combustion system was constructed using quartz tubing. This is essential for building a prototype, since a visual check is needed for incomplete soot oxidation in the tube. Breakable tubing, however, would not be desirable in a portable-use instrument. It was considered that for routine use a combustion tube made of Inconel 601 alloy or a ceramic such as mullite would be appropriate. The actual geometric arrangement can take various forms; for simplicity it will be assumed that a long straight tube is used as the combustion chamber. Taking a 30 s residence time requirement and a flow rate of 1.3 cm³/s gives a required volume of 40 cm³, which can be met by using a tube with an i.d. of 16 mm and a length of 200 mm. In practice, the 200 mm length would probably be increased to 300 mm to provide some additional residence time to ensure combustion completeness. These values are practical.

The simple cylindrical tube shape used in the NIST development work does not represent the only combustion chamber that can be considered. In our studies the oxygen flow, as indicated in Fig. 1, opposed the sampled flow, resulting in a flame forming near the oxygen inlet for φ greater than 1. This flame assisted in the conversion of the sampled combustion products including smoke particulate, unburned hydrocarbons, and CO to CO₂ and H₂O. For some applications it would be more convenient to place the oxygenator stream inlet at the entry of the combustor, though there may be less efficient conversion of the products to CO₂ and H₂O and there is also the possibility of combustion instability resulting from the heating of a combustible mixture as it flows down the combustion tube. Both combustor shapes and catalyst geometry could well be varied in optimizing the completeness of combustion for highly sooting samples.

The heated inlet tube should have a diameter of ~ 6 mm. Larger tube diameters are not needed and would slow down the response of the system. Smaller diameter tubes, however, normally cannot be used because of a tendency to get clogged with soot.

The system for removing H₂O and CO₂ from the line going to the oxygen analyzer can be designed according to accepted methods.¹⁴ It is important to take account of the

fact, however, that sustained levels of combustion products that must be removed may be substantially greater than in some common current oxygen measuring systems. If rapid time response of the system is desirable in a particular application, excessively large volumes should not be used for the H₂O and CO₂ removal traps. Some scrubber arrangements can be particularly prone to soot clogging should operating limits of the instrument be exceeded and unburned soot break through past the combustor. Thus, in most cases, a soot filter immediately upstream of the first trapping device should be present.

The prototype phi meter, as designed, was intended for relatively short sampling periods ($< \sim 1$ h). The single-run operating time is limited by the time period required to saturate the H₂O and CO₂ removal media. For use in situations where extended-period monitoring is required, different arrangements would need to be made. These could take the form of different arrangements for the scrubbing media being adopted. For example, if fast system response time is not required, very large containers of scrubbing media could be used. Alternatively, for certain monitoring applications a periodic-sampling (start/stop) scheme might be implemented.

A practical, portable instrument will also need to incorporate a portable system for calibration and a convenient means for determining the end of the lifetime of the catalyst. These features will need to be provided by a manufacturer making an instrument based on the principles described.

IX. DISCUSSION

A novel instrument has been developed for portable, modest-cost monitoring of combustion stoichiometry. The measuring principle is based on oxygen consumption. This is especially attractive since it does not require calibrations or adjustments specific to the fuel type being used. The operating range is approximately centered on $\varphi = 1$. The NIST prototype instrument showed successful operation for mixtures as rich as $\varphi = 3$. For richer yet mixtures, a more optimized arrangement for the catalytic combustor would be needed. At the low- φ end, no systematic deviation was seen even for $\varphi = 0.1$.

The initial applications have been toward quantifying the stoichiometry of experimental room fires being studied as a fire safety engineering topic. Hitherto, the equivalence ratio in such fires was difficult to determine, since fuel composition may not be known and both air and fuel flow rate measurements are typically subject to major uncertainties. The new instrument has been demonstrated to function well in characterizing such fires. For broader application, we see its utility as a general combustion diagnostic method. The phi meter will find application in various situations where a combustion process needs to be quantitatively studied but a full range of monitoring instrumentation has not been installed.

ACKNOWLEDGMENTS

Dr. William M. Pitts was instrumental in making arrangements for the development of this project. The contri-

butions of experimental measurements by Nelson Bryner and Emil Braun were valuable in validating the operation of the phi meter.

APPENDIX: φ EQUATION FOR CONSTANT INLET AIRFLOW

The normal operation of the phi meter is to have constant flow at the outlet. For calibrating the system, it was convenient to have a constant inflow of air and to adjust φ by varying the inlet flow of fuel. For the case of constant inlet flow of air and added oxygen to the oxygenator but no fuel flow, we obtain the following expression for the mole fraction of oxygen:

$$X_{O_2}^i = \frac{\dot{n}_{O_2}^a + \dot{n}_{O_2}^0}{\dot{n}_{O_2}^a + \dot{n}_{O_2}^0 + \dot{n}_{N_2}^0} = \frac{\dot{n}_{O_2}^a + \dot{n}_{O_2}^0}{\dot{n}_{O_2}^a + \dot{n}_{O_2}^0 + [(1 - X_{O_2}^0)/X_{O_2}^0]\dot{n}_{O_2}^0} \quad (A1)$$

From Eq. (13), we see that φ_1 can be expressed as

$$\varphi_1 = \frac{\dot{n}_{O_2}^a}{\dot{n}_{O_2}^0} \quad (A2)$$

Dividing the numerator and denominator of Eq. (A1) by $\dot{n}_{O_2}^0$, we obtain

$$X_{O_2}^i = (\varphi_1 + 1) \left/ \left(\varphi_1 + 1 + \frac{1 - X_{O_2}^0}{X_{O_2}^0} \right) \right. \quad (A3)$$

Solving Eq. (A3) for φ_1 , we find

$$\varphi_1 = \frac{X_{O_2}^i - X_{O_2}^0}{X_{O_2}^0(1 - X_{O_2}^0)} \quad (A4)$$

The expression for φ , given by Eq. (28), is obtained from the sum of φ_1 and the expression for φ given by Eq. (9), which corresponds to no oxygen addition.

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